

## **REMARKS/ARGUMENTS**

This Reply is in response to the Office Action dated November 18, 2003. This Reply is filed along with a petition for a one-month extension of time and authorization to charge the required statutory fee to Deposit Account No. 50-0951.

Claims 1-48 were pending at the time of the Office Action. All claims were rejected. In this Reply, claims 1-8, 22, 23, 47, and 48 have been amended and claims 27 and 28 have been canceled. The amendments are provided in the Listing of Claims herein to reflect the claims as amended. No new matter has been added.

The Examiner objected to the specification because the specification (Example section) on page 65, line 17 recited "5% Hydrogen peroxide". In response, the specification has been amended to now recite 5 wt. %. Accordingly, the objection to the specification is overcome.

The Examiner rejected claim 23 under 35 U.S.C. §112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention due to the recital of trademark named surfactants. In response, Applicant has amended this claim to replace the trademark names with their associated chemical compositions. Accordingly, the 35 U.S.C. §112, second paragraph rejection of claim 23 is now overcome.

Turning to rejections based on art, claims 1-16, 18-23, and 31-48 were rejected under 35 U.S.C. §102 (b), as being anticipated by U.S. Patent No. 5,954,997 to Kaufman. The Examiner rejected claim 17 under 35 U.S.C. 103(a) as being unpatentable over U.S. Patent No. 5,954,997 to Kaufman as applied to claim 1 and further in view of U.S. Patent No. 6,454,819 B1 to Yano et

al. The Examiner also rejected claims 24-30 under 35 U.S.C. 103(a) as being unpatentable over U.S. Patent No. 5,954,997 to Kaufman as applied to claim 1 and further in view of U.S. Patent No. 6,436,811 to Wake et al.

According to the Examiner:

Kaufman uses the a CMP slurry that contains abrasive materials (same as applicants' composite particles) and an optional additive such a surfactant (same as applicants' adsorption additive) that "may be produced using conventional techniques... Typically, the oxidizing agent and other non-abrasive components, are mixed into an aqueous medium, such as deionized or distilled water, ..." (column 8, lines 43-49), then using Kaufman slurry in the same manner as the claimed invention would inherently result in a slurry chemical mechanical polishing (CMP) of a structure including a refractory metal based barrier film and a dielectric film, comprising: a plurality of composite particles and at least one selective adsorption additive, said composite particles including an inorganic core surrounded by a shell including said selective adsorption additive, wherein said selective adsorption additive is substantially adsorbed by said dielectric film but not substantially adsorbed by said refractory metal based barrier film, in claim 1.

Before reviewing the cited art, Applicant will first review the claimed invention as now recited in amended claim 1 and some background regarding micelle formation. The review of micelle formation and associated details in essentially equivalent to that presented in for which a the Reply to Office Action was filed on February 2, 2004 in related application No. 10/255,493 entitled HIGH SELECTIVITY AND HIGH PLANARITY DIELECTRIC POLISHING. '493 is also assigned to the present Examiner.

Amended claim 1 recites a slurry for chemical mechanical polishing (CMP) of a structure including a refractory metal based barrier film and a dielectric film. The slurry includes a bulk solution, a plurality of composite particles including an inorganic core surrounded by a shell including a selective adsorption additive. The selective adsorption additive is in a concentration from 6 to 1,000 critical micelle concentration (CMC) when the selective adsorption additive is non-ionic (uncharged) and from 1 to 1,000 CMC when the selective adsorption additive is

zwitterionic, anionic or cationic (charged). Applicant has found that cationic, anionic and zwitterionic surfactants are particularly effective in achieving selective adsorption and resulting improved polishing performance since charged surfactants have demonstrated stronger adsorption as compared to uncharged (nonionic) surfactants.

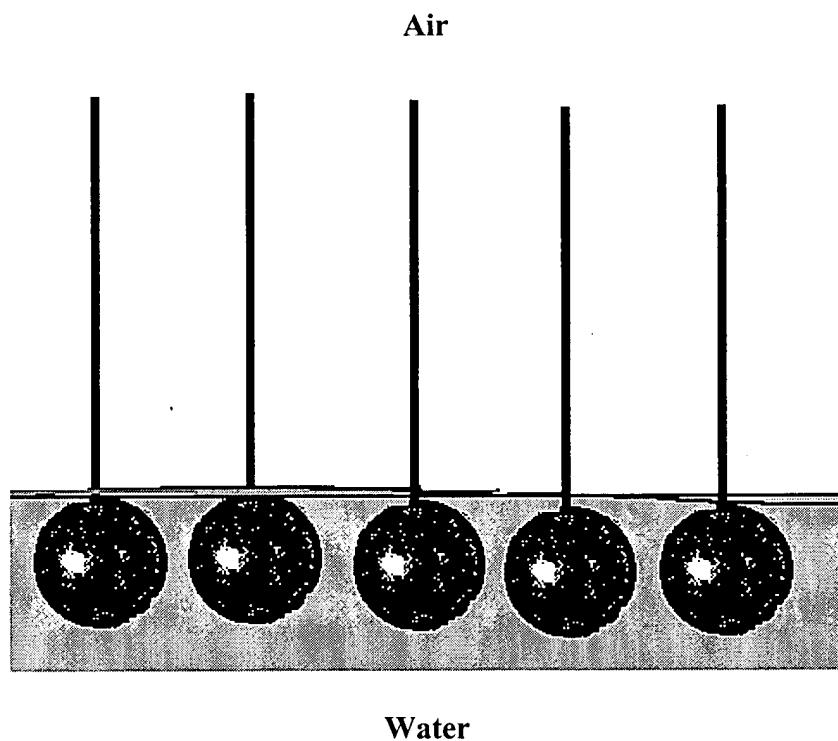
To understand the invention, a clear description of Critical Micelle Concentration (CMC) is first presented. Certain molecules may be said to contain two distinct components, differing in their affinity for solutes. The part of the molecule which has an affinity for polar solutes, such as water, is said to be hydrophilic. The part of the molecule which has an affinity for non-polar solutes, such as hydrocarbons, is said to be hydrophobic. Molecules containing both types of components are said to be amphiphilic.



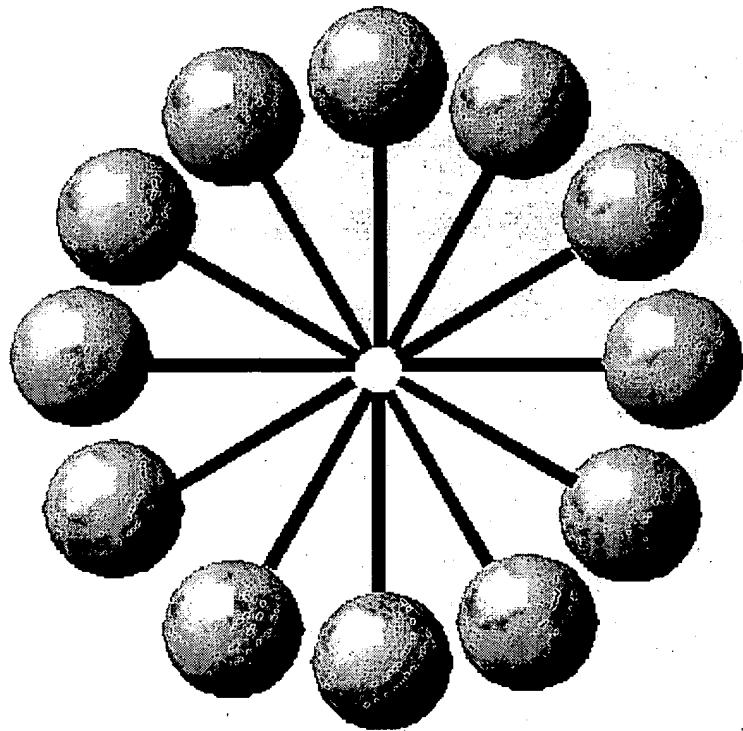
hydrophobic      hydrophilic

For example, amphiphilic molecules display distinct behavior when interacting with water. The polar part of the molecule "seeks" to interact with water while the non-polar part "shuns" interaction with water. There are two ways in which such a molecule achieve both these states.

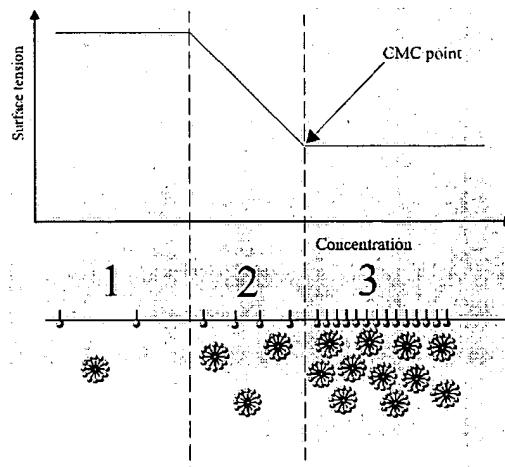
An amphiphilic molecule can arrange itself at the surface of the water such that the polar part interacts with the water and the non-polar part is held above the surface (either in the air or in a non-polar liquid) as shown below. The presence of these molecules on the surface disrupts the cohesive energy at the surface and thus lowers the surface tension. Such molecules are called "surface active" molecules or surfactants.



Another arrangement of these molecules can allow each component to interact with its favored environment. Molecules can form aggregates in which the hydrophobic portions are oriented within the cluster and the hydrophilic portions are exposed to the solvent. Such aggregates are called micelles. An example of a spherical micelle is diagrammed on the next page.



The proportion of molecules present at the surface or as micelles in the bulk of the liquid depends on the concentration of the amphiphile. At low concentrations surfactants will favor arrangement on the surface. As the surface becomes crowded with surfactant more molecules will arrange into micelles. At some concentration the surface becomes completely loaded with surfactant and any further additions must arrange as micelles. This concentration is called the Critical Micelle Concentration (CMC). It follows that measurement of surface tension may be used to find CMC. A graph of surface tension vs. log of concentration of surfactant added will appear as follows:



In this graph three phases can be seen:

- 1) At very low concentrations of surfactant only slight change in surface tension is detected.
- 2) Additional surfactant decreases surface tension
- 3) Surface becomes fully loaded, no further change in surface tension results.

Returning again to the claimed invention, when the surfactant concentration in the slurry is above some threshold level above 1 CMC, some layers will experience substantial adsorption where the CMP polishing rate (for a given slurry and CMP polishing conditions) without the adsorption additive is substantially more (e.g. at least 4 times or more) than the CMP polishing rate when the slurry includes the adsorption additive/additives. On the other hand, other layers will experience non-substantial adsorption relative to a given film without the adsorption additive being substantially less (e.g. less than 4 times) than the polishing rate of the layer when the slurry includes the selective adsorption additive/additives. As a result, polishing selectivity and resulting planarity can be significantly improved over conventional slurries and important newly discovered and important effects can be exploited.

Now turning to the principal cited art, Kaufman discloses a first CMP slurry including an abrasive, an oxidizing agent, a complexing agent, a film forming agent and an organic amino

compound, a second polishing slurry including an abrasive, an oxidizing agent, and acetic acid. The weight ratio of the oxidizing agent to acetic acid is at least 10. A method for using the first and second polishing slurries sequentially to polish a substrate containing copper and containing tantalum or tantalum nitride or both tantalum and tantalum nitride is also disclosed.

Although Kaufman discloses the slurry can include one or more surfactants, as noted below in the excerpt from col. 6, line 45 to col. 7, line 12, Kaufman's surfactant is provided only for stabilizing the slurry to avoid settling, flocculation or decomposition, not for selective adsorption. Micelle formation and selective adsorption is not mentioned by Kaufman. The maximum surfactant concentration disclosed by Kaufman is from .001 wt % to a maximum of 0.2 % by weight, which is generally an insufficient concentration to achieve micelle formation to realize the selective adsorption effect provided by Applicant's claimed slurry. Col. 6, line 45 to col. 7, line 12 of Kaufman is copied below for convenient reference:

In order to stabilize the first CMP slurry against settling, flocculation, and decomposition, a variety of optional CMP slurry additives, such as surfactants, stabilizers, or dispersing agents, can be used. If a surfactant is added to the first CMP slurry, then it may be an anionic, cationic, nonionic, or amphoteric surfactant or a combination of two or more surfactants can be employed. Furthermore, it has been found that the addition of a surfactant may be useful to reduce the within-wafer-non-uniformity (WIWNU) of the wafers, thereby improving the surface of the wafer and reducing wafer defects.

In general, the amount of additive such as a surfactant that may be used in the first CMP slurry should be sufficient to achieve effective stabilization of the slurry and will typically vary depending on the particular surfactant selected and the nature of the surface of the metal oxide abrasive. For example, if not enough of a selected surfactant is used, it will have little or no effect on first CMP slurry stabilization. On the other hand, too much surfactant in the CMP slurry may result in undesirable foaming and/or flocculation in the slurry. As a result, stabilizers such as surfactants should generally be present in the slurry of this invention in an amount ranging from about 0.001% to about 0.2% by weight, and preferably from about 0.001 to about 0.1 weight percent. Furthermore, the additive may be added directly to the slurry or treated onto the surface of the metal oxide abrasive utilizing known techniques. In either case, the amount of additive is adjusted to achieve the desired concentration in the first polishing slurry. Preferred surfactants useful in the first

CMP slurry include dodecyl sulfate sodium salt, sodium lauryl sulfate, dodecyl sulfate ammonium salt, and mixtures thereof. Examples of preferred surfactants include TRITON DF-16 manufactured by Union Carbide, and SURFYNOL manufactured by Air Products and Chemicals.

Although 1 CMC is theoretically sufficient to form micelles, the presence of additional slurry components, particularly slurry particles, raises the minimum surfactant concentration level to form micelles to some higher level, such as at least several CMC. Accordingly, for ionic surfactants (cationic, anionic, and zwitterionic), Kaufman's disclosed surfactant concentration range (less than 1 CMC) is by definition insufficient to form micelles and achieve the advantages provided by Applicant's invention, while it is unclear whether Kaufman's maximum concentration provided for nonionic surfactants is sufficient to form micelles. Accordingly, Applicant respectfully disagrees with the Examiner's inherency assertions regarding selective adsorption (page 4) and pressure dependant adsorption (page 7) as both of these conditions require a minimum selective adsorption additive concentration necessary to achieve the claimed selective adsorption additive self assembly in bulk solution.

Applicant has below provided is a listing of the specific surfactants disclosed by Kaufman expressed in terms of the equivalent CMC for Kaufman's maximum disclosed surfactant concentration of 0.2 wt %.

<u>Surfactant</u>	<u>CMC by weight %</u>	<u>0.2 wt % conversion to CMC</u>
dodecyl sulfate sodium	0.237	0.84 CMC
sodium lauryl sulfate	0.230	0.87 CMC
dodecyl sulfate ammonium salt	0.214	0.93 CMC
TRITON DF 16	0.04	5.0 CMC
SURFYNOL (examples shown below)		
Surfynol EP-810	0.9	0.22 CMC
Surfynol EP-830	2.9	0.07 CMC

The TRITON DF 16 surfactant is the only Kaufman surfactant in which Kaufman's disclosed maximum surfactant concentration of 0.2 wt % corresponds to more than 1 CMC, that

being 5.0 CMC. However, TRITON is a family of nonionic surfactants. The other surfactants above disclosed by Kaufman are all anionic surfactants. As shown above, Kaufman's disclosed maximum surfactant concentration of 0.2 wt % corresponds to less than 1 CMC for surfactants which are other than non-ionic surfactants, specifically the "charged surfactants" comprising anionic, cationic and zwitterionic surfactants. Thus, by definition, micelle formation for the group of charged surfactants based on the teachings of Kaufman is not possible.

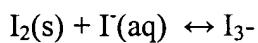
As noted above Claim 1 has been amended to recite a selective adsorption additive concentration of between 6 and 1,000 CMC for nonionic selective adsorption additives and between 1 CMC and 1,000 CMC for anionic, cationic and zwitterionic selective adsorption additives. Support for this limitation can be found on page 15, lines 13 to 18 in light of MPEP 2163.05 III entitled RANGE LIMITATIONS. The claimed surfactant concentration range is outside Kaufman's disclosed surfactant range and generally permits surfactant self assembly to form structured layers in a bulk solution of a slurry and the resulting desired selective adsorption effects. The other cite references do not make up for the above-described deficiencies regarding Kaufman. Accordingly, Applicant submits that amended claim 1 and all claims dependent thereon are patentable over Kaufman.

Certain dependent claims are believed to recite additional patentable limitations. For example, amended claim 6 now recite the particles comprise nanoporous particles, while claim 7 now recites the particles are multiphase particles comprising a first material coated with a second material, the second material being different from the first material. Both these particle types provide unexpected highly advantageous results when used in conjunction with Applicant's claim surfactant comprising slurry.

Specifically, regarding nanoporous particles, because of the porous structure of the particle surface, the adsorption of surfactants or polymer additives can occur at different, and generally lower, concentrations as compared to bulk particles. Kaufman does not disclose or suggest nanoporous particles as Kaufman teaches using surfactants to only stabilize the slurry.

Regarding multiphase particles, the coating allows control of the strength and density of the selected adsorption additive adsorption by controlling the thickness, morphology and composition of the coating. Specifically, if specific coated particles (e.g. alumina coated silica, or silica coated alumina) are included in Applicant's surfactant comprising slurry, the selective adsorption phenomena may occur at a lower concentration than with standard bulk particles. Thus, selective adsorption effects can be obtained at different CMCs as compared to when bulk particles are used. As with the nanoporous particles, Kaufman does not disclose or suggest multiphase particles as Kaufman teaches using surfactants to only stabilize the slurry.

Amended claim 8 now recites the slurry includes at least one species selected from the group consisting of a polyhalide ion, or the halogens I<sub>2</sub>, Br<sub>2</sub> or F<sub>2</sub>. The term "halogen" is used in the application and is also well known in solution chemistry and refers to diatomic Group VIIA molecules, such as I<sub>2</sub>, Br<sub>2</sub> or F<sub>2</sub>. Halogens in solution generally produce characteristic colors to the solution, such as a purple color when Br<sub>2</sub> is present. The phrase "polyhalide ion" is also well defined in solution chemistry as a molecular ion including at least two Group VIIA species, the species not necessarily being different, such as I<sub>3</sub>. Although the term "polyhalide ion" is not disclosed in the application, it is well known in solution chemistry that the mixing of a halogen with a halide ion forms a polyhalide ion, such as:



Polyhalide ions can be contrasted with halide ions, which are also well defined and refer to monoatomic ions, such as  $F^-$ ,  $Cl^-$  and  $Br^-$ . Halide ions are not known to impart color to a solution.

The recited polyhalide ion or halogen species reacts with metal films, such as copper or silver films, to form a soft layer on a surface of the film. The soft layer can be  $AgI$ ,  $CuI$ ,  $AgBr$  or  $CuBr$ , for example. Such metal halide layers are soft layers as they have a hardness less than that of the associated metal film. This facilitates a low defect CMP process, such as that obtainable using soft particles which have a hardness less than the metal layer being polished in the slurry.

The invention may be contrasted with conventional copper CMP slurries which include oxidizers, such as  $KIO_3$  which form a copper oxide layer using the strongly oxidizing iodate ion ( $IO_3^-$ ). Specifically, a copper oxide ( $Cu_2O$  or  $CuO$ ) layer is formed on the surface of the copper (or silver film) during the CMP process. Copper oxide ( $Cu_2O$ ) is known to have a Mohs hardness of 3.5 to 4 and  $CuO$  to have a Mohs hardness of 3.5 to 4, which are both substantially greater than the Mohs hardness of copper films (2.5 to 3) or silver films, or common underlying dielectric layers such as silicon dioxide. Thus, the invention substantially overcomes problems associated with copper and silver CMP which relates to the need for abrasive particles to polish the hard oxide surfaces formed by the oxidizing species in the slurry. Specifically, the formation of a soft surface layer having a hardness less than the metal film, as opposed to a hard oxide film, permits a reduction in dishing, erosion, surface scratching, peeling, and also a reduction in the polishing of underlying layers. Since no cited reference discloses or suggests addition of a polyhalide ion,  $I_2$ ,  $Br_2$  or  $F_2$  to a slurry for CMP, Applicant submits that amended claim 8 recites independently patentable subject matter.

Applicant has made every effort to present claims which distinguish over the cited art, and it is believed that all claims are now in condition for allowance. However, Applicant requests that the Examiner call the undersigned (direct line (561) 671-3662) if anything further is required by the Examiner prior to issuance of a Notice of Allowance for all claims.

The Commissioner for Patents and Trademarks is hereby authorized to charge \$55.00 for a one-month extension of time and any deficiency in any fees due with the filing of this paper or credit any overpayment in any fees paid on the filing, or during prosecution of this application to Deposit Account No. 50-0951.

Respectfully submitted,



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